

AIR-POLLUTION DUE TO  
AUTOMOTIVE EMISSION

by

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B. E. (Mech.) Gujarat University, India, 1967

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A MASTER'S REPORT

submitted in partial fulfillment of the

requirements for the degree

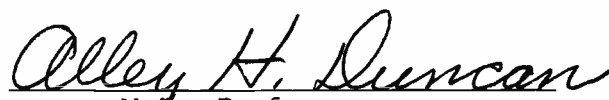
MASTER OF SCIENCE

Department of Mechanical Engineering

KANSAS STATE UNIVERSITY  
Manhattan, Kansas

1968

Approved by:

  
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## INTRODUCTION

This report discusses the causes, effects and controls of air pollution due to automotive emission. Air pollution presents a seriously increasing threat to the health and welfare of people in areas of large population. One principal contributor to this pollution is the emission of carbon monoxide, hydrocarbons, nitrogen oxides and lead components from the exhaust of automotive vehicles.

The United States Department of Health, Education and Welfare estimates that 142,000,000 tons of pollutants are dumped into the atmosphere each year. Of this approximately 86,000,000 tons/year is attributed to the exhaust of automotive vehicles. Table 1 (2) below shows the various sources of air pollution and the comparative amounts from each source. Also shown in the table is the breakdown of constituents (carbon monoxide, etc.), that are produced by the combustion of hydrocarbon fuels in internal combustion engines.

Table 1: Total U.S. Air Pollution

Source	Tons/Year	% of total		Tons/Year
Industry	23,000,000	16.8%		Carbon monoxide 66,000,000
Power plants	20,000,000	14.1%		Oxides of Nitrogen 6,000,000
Motor-vehicles	86,000,000	60.6%	→	Hydrocarbons 12,000,000
Space heating	8,000,000	5.6%		Sulfur dioxides 1,000,000
Refuse disposal	5,000,000	3.5%		Lead Compounds 190,000
	142,000,000			Particulates 1,000,000

The importance of the problem is also illustrated by comparison of the pollution data in table 2. These data were taken from the California State Department of Public Health<sup>1</sup> and U.S. Department of Health Education and Welfare<sup>2</sup> and the tabulation indicates the high percentage of pollution in three large cities due to motor-vehicles. Other large metropolitan areas would show similar pollution percentages.

Table 2. Emissions Source Comparisons - 1965

Area	Carbon Monoxide		Hydrocarbon		Oxides of Nitrogen	
	Percent		Percent		Percent	
	From Motor	Non-motor	From Motor	Non-motor	From Motor	Non-motor
Los-Angeles <sup>1</sup>	97	3	72	28	65	35
San Francisco Bay area <sup>1</sup>	78	22	51	49	57	43
St. Louis Interstate area <sup>2</sup>	97	3	62	38	32	68

At present several Government agencies and private organizations are actively in search of satisfactory solutions to the problem. The effects of aggregate air pollution on health and welfare are being studied. Even though technology is known for the control of exhaust emission from gasoline internal combustion engines, still much research is needed to develop a practical and economical control of such air pollution.

The purpose of this report is to review the problem and its causes and to describe the several solutions that seem plausible.

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<sup>1</sup>Source: California State Department of Public Health

<sup>2</sup>Source: U.S. Department of Health, Education and Welfare, Interstate Air Pollution Study, 1966.

## 2. SOURCES OF AIR POLLUTION

It is common for people to think that passenger cars, buses and trucks produce a different type of exhaust emission. This is partially true because the type of engine makes some difference. The type of vehicle in which an engine is used influences to a certain extent the kind of pollution and this is due to change in load, speed, temperature and other operating factors.

Generally, hydrocarbon fuels are used in internal combustion engines. These fuels are burned in the cylinder of an engine to convert chemical energy into mechanical energy. To burn the fuel, air is needed as the source of oxygen required to combine chemically with carbon and hydrogen; and in this combination, heat is produced and high pressure is developed. The high pressure in turn drives the piston and thereby turns the crank shaft and ultimately propels the vehicle.

When the hydrogen and carbon of the engine fuel combine with oxygen of air, water vapor and carbon dioxide are formed. Both of these products of ideal and complete combustion are harmless. But unfortunately, for one reason or the other, combustion is not complete and the products of imperfect combustion are the prime cause of the motor-vehicle air-pollution problem. One of these products is carbon monoxide. And carbon monoxide is dangerous. Many other substances are also produced but they are in very small quantities. Certain additives are mixed with fuel for improved engine performance and life. These additives undergo chemical changes during combustion. When engine maintenance is poor some lubricating oil is pumped into the cylinder, and it burns giving blue smoke.

Besides exhaust system emissions, crankcase emissions also contribute to pollution. Crankcase emissions are composed of (1) engine blow-by gasses (2) ventilation air, and (3) crankcase lubricant fumes. From the air pollution standpoint, the most important of these is blow-by. A small amount of the gases in the combustion chamber escapes past the pistons into the crankcase, mostly during the compression stroke. These blow-by gases are composed of approximately 70 to 80 percent fresh air-fuel mixture and the remainder is the residue combustion products of the previous cycle. The quantity of blow-by gases is influenced by engine design and by operating variables.

Emission due to evaporation of gasoline from the tank for the most part is composed of only the more volatile hydrocarbons in gasoline. These losses occur continuously whether the vehicle is parked or in operation. The principal tank emission governing factors are the volatility of the gasoline and the ambient temperature. Moreover the rate of evaporation is increased as the tank liquid level drops. Sealer and pressurizer fuel systems and vapour collection systems help to reduce the tank emission.

Carburetor-evaporation gasoline emissions also can be separated into "running losses" which occur during vehicle operation and "hot soak" losses by evaporation with the vehicle parked. In this case also the amount of emission is governed by gasoline volatility and by the surrounding temperature. Carburetor design, engine compartment layout, and body sheet-metal configuration also influence the magnitude of emission.

A gasoline engine compresses a premixed charge of air and fuel

vapor prepared by the carburetor. To burn the fuel, this charge is ignited by an electric spark. Combustion is most efficient when there is slightly less fuel than can be burned completely with the available air. In this case the emission of pollutant is minimum. Therefore, carburetors are designed to deliver a lean mixture when the engine operates at steady state and part load. Maximum power is obtained with a mixture that is slightly richer than ideal, that is, when there is more fuel than can burn with the available air. In this situation emission of pollutants is significant. Emission of pollutants in this case is high, but in city traffic, since full power is used rarely and briefly, this condition does not cause serious concern. At idle and during acceleration it is necessary to operate with rich mixtures. During deceleration when the throttle is closed, emission is significant. At this time little air reaches the cylinder, but fuel flow remains high during the early part of deceleration process and so combustion is poor.

The diesel engine differs from the gasoline engine in that, it uses heavier i.e., less volatile fuels, it compresses air only instead of fuel air mixture, fuel is injected into the cylinders at about the same time at which the electric spark occurs in the gasoline engine and the injected fuel autoignites by contact with the air that has been heated by compression. The important difference is that combustion does not take place in a homogeneous mixture as it does in the gasoline engine, but around and within the fuel spray as it is injected. Therefore mixing of fuel and air is incomplete. Some of the fuel burns with

insufficient oxygen. To prevent this, various combustion chamber designs are in use which help mixing, and less fuel is injected than can be burned theoretically in the available air.

When there is insufficient oxygen for combustion, carbon is formed and this carbon appears in diesel exhaust smoke. Due to incomplete combustion some of the fuel energy is wasted and air pollution occurs. The smoking exhaust of a diesel engine indicates that it is either poorly maintained or that someone, in order to obtain a little extra power has adjusted the engine to receive more fuel than needed. Poor maintenance may result in a clogged air filter with the engine receiving less air than needed. Poor atomization and distribution of fuel will also result in incomplete combustion. At part load, a diesel seldom smokes because to reduce its output, only the fuel supply is reduced, and the proportion of air in the combustion chamber increases, while in gasoline engines both air and fuel are throttled proportionately so as to maintain a constant fuel-air ratio.

Because the carbon-monoxide production of diesel engines is practically zero, at least as long as there is no smoke, they are not a serious problem. As soon as smoke appears, carbon monoxide appears and both increase together.

Other exhaust constituents are not vastly different from those of gasoline engines. Oxides of nitrogen are produced in somewhat greater quantities, while unburned hydrocarbons are nearly absent (13).

Diesel blow-by gases contain only small quantities of pollutants because the diesel compresses air only, and since the diesel uses less volatile fuels, the evaporation loss from the fuel tank is negligible.



Diesel fuel systems are closed, so there is no escape path for fuel vapors. Because of the small number of diesel engines, and their relatively small pollutant emission the research on diesel emissions has been limited.

A great deal is still to be learned about emissions of gasoline engines. Only since the mid-fifties has a broader awareness of the contribution of motor vehicle emissions to air pollution been developed. As most of the constituents of air pollutants occur in such low concentrations that they must be measured in ppm (parts per million), the early attempts to understand the character and the role of exhaust emissions were hampered by lack of instruments capable of detecting and measuring the various constituents.

The total emission of pollutants from a single vehicle is not very large. It is the concentration of a great number of vehicles in any one area, particularly in cities, that creates the problem.

### 3. VARIOUS COMPONENT GASES OF ENGINE-GENERATED POLLUTION:

Generally air-pollution is characterized by a decrease in visibility, crop damage, eye irritation, objectionable odor, smog formation and rubber deterioration. All these effects are due to different pollutants in automotive emission. To study these pollutants, an exhaust gas-sample should be collected but this is difficult when the automobile is moving and four driving conditions are to be considered:

1. Acceleration (full throttle)
2. Steady driving
3. Deceleration
4. Idling - normal idle

Stanford Research Institute used a mass spectrometer analysis to estimate the nature and amounts of air pollutants exhausted by passenger cars into the Los Angeles County atmosphere (4). But to collect the automobile exhaust gas sample, the apparatus shown in the figure 1 was used. This apparatus was mounted in a trailer drawn by the test vehicle. The automobile exhaust was connected to the trailer in a double tube to guard against condensation of water. The sample was taken from the inner tube in a 250 ml. sample bottle, which had been previously evacuated, by raising the pressure in the bottle from 1 to 100 mm. mercury with the exhaust gas. In this way 20 to 40 samples of exhaust emitted during each driving condition were collected and analyzed. In the laboratory use of the orsat-apparatus can be made instead of the mass spectrometer, and this permits a more rapid analysis. It saves time and it also gives fair accuracy.

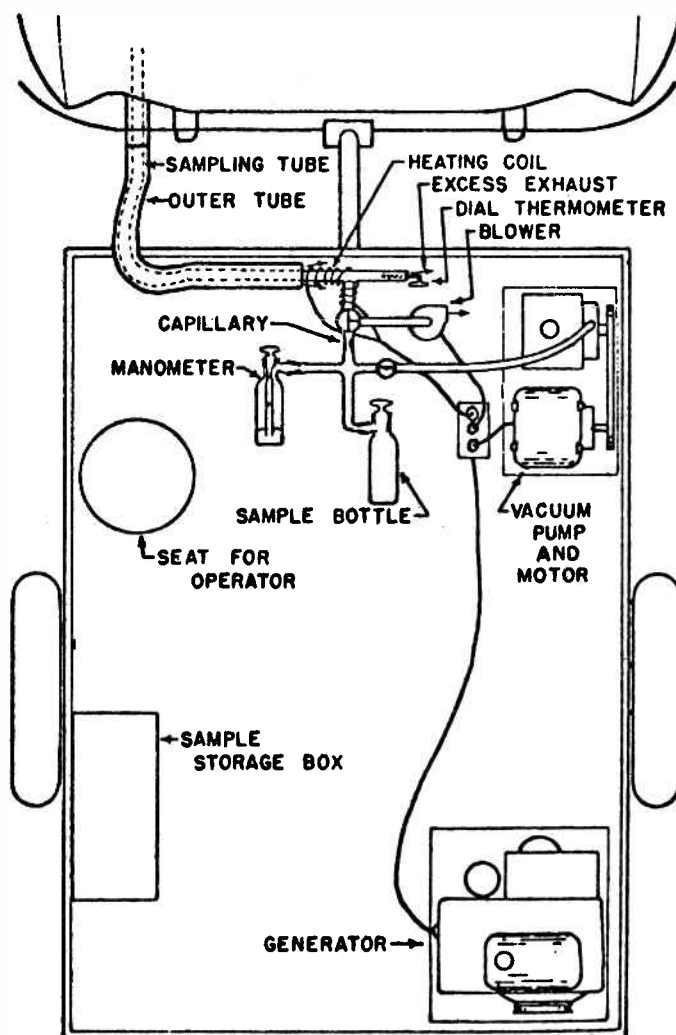


Fig. 1. Apparatus used for automobile exhaust sampling

The exhaust gas-analysis shows that the exhaust gas can contain unburned hydrocarbons, oxides of nitrogen, carbon monoxide, carbon dioxide, particulate matter, lead, odor and oxides of sulphur.

In the presence of ultraviolet radiation or sunlight energy, unburned hydrocarbons and oxides of nitrogen produce smog. The reactivity of hydrocarbons and their derivatives in this photosynthesis reaction is a function of their chemical structure. The spark ignition engine produces a greater quantity of unburned hydrocarbons than the compression ignition engine, but the reactivity of the hydrocarbons from C.I. engine is twice that from the spark ignition engine.

The route to smog formation is shown in figure 2. These 13 equations are involved and represents chemical reactions believed to occur in the atmosphere (14). These reactions occur simultaneously, and in many instances the products of one reaction furnish the reactants for another. In some cases these reactions regenerate some of the original reactants to give a chain reaction.

Generally only nitric oxide is produced in the exhaust of I.C. engines but the reactive material in photocatalysis is nitrogen dioxide. Nitrogen dioxide is formed by the oxidation of the nitric oxide. Hydrocarbons and many other engine variables influence the concentration of nitric oxide.

Carbon monoxide is a poisonous gas and it should be reduced to a minimum whenever possible. Since the concentration of carbon monoxide follows directly the fuel-air ratio, a rich mixture operation should be avoided at all times (15).

Solid particles are usually carbon particles. But they may also

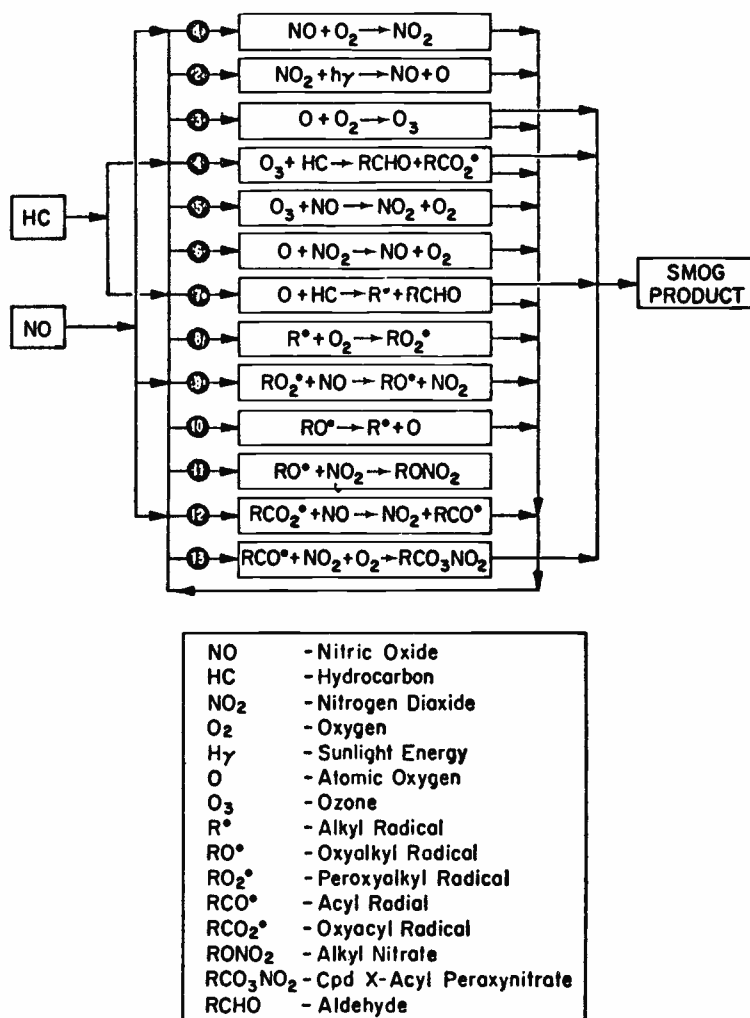


Fig. 2. Route of photochemical smog formation tracing the reactions of hydrocarbons and nitric oxide in the presence of oxygen and sunlight. Thirteen equations are involved.

be products of lead-alkyl decomposition. These particles are undesirable because they produce surface contamination and they also act as the nuclei for the condensation of vaporous materials into droplets. The diesel engine is a main producer of odors from the presence of aldehydes. To reduce odors, it is necessary to reduce unburned hydrocarbons. In exhaust gases, sulphur exists primarily as sulphur dioxide. The concentration of sulphur dioxide is directly proportional to the sulphur content of the fuel. The presence of sulphur dioxide creates discomforts of bronchial and nasal irritation; and aerosol formation reduces visibility (6).

From the above studies it can be observed that pollutants from the moment of their release are subjected to the action of natural components of air or they may react with other pollutants. Photochemical and other reactions change normally harmless compounds into objectionable compounds or products. On the other hand, substances irritating when released may soon be converted into harmless ones.

#### 4. THE EFFECTS OF AIR-POLLUTION

##### 1. Human Health:

In the past, public action in the prevention of disease has usually awaited the identification of a single causative agent. This pattern of thinking and response is inappropriate to combat the bad health effects associated with air pollution.

Much speculation and controversy about whether or not air pollution causes disease is irrelevant to the significance of air pollution as a public health hazard. There is frequently a simple association between an infectious disease agent and the acute disease reaction. The idea that one factor is wholly responsible for any one illness is patently too simple to provide all the answers to deal with chronic diseases (10).

Chronic bronchitis, in England is established as a specific disease entity. It develops over a long period of time and can become crippling through a combination of many factors - air pollution, smoking, repeated and recurring bouts with infectious agents, occupational exposures - all affected, perhaps by an hereditary predisposition. There is probably no single cause of chronic bronchitis, but there is sufficient evidence that air pollution can and does contribute to its development.

Although the present state of knowledge with respect to the effects of air pollution is characterized by large gaps in information, data are available which can serve as a basis for action until more definitive studies are completed. Epidemiological research on the effects of air pollution on human populations has been under way for the past decade.

There still are deficiencies in scientific knowledge of relationship between air-pollution and respiratory disease. A need exists for more quantitative information - for more precise data concerning the pollutants which affect human health and in what amounts and what conditions they produce their effects. But the qualitative evidence is conclusive. There is no doubt that air pollution is a factor which contributes to illness, disability and death from chronic respiratory diseases (18).

Cigarette smokers and those with lung and heart disorders are thought to be in greatest danger from contaminated air.

The killing and disabling potential of aggregate community air pollution from a variety of sources has been strikingly demonstrated in repeated episodes of acute pollution which have occurred both in this country and abroad. The air-pollution catastrophe in London from December 5 through December 9, 1952 took an estimated 3500 to 4000 lives. The episodes in Donora, Pennsylvania, in 1948, Meuse Valley, Belgium in 1930, and New York City in 1953 and 1966 are other well known examples of the dangers and discomforts which result from adverse meteorological conditions and crowded populations (17). These dramatic occurrences were primarily due to non-automotive sources of air pollution, but they serve as a reminder that clean air is a precious natural resource. While man's daily consumption of food and water totals approximately seven pounds, he requires about thirty pounds of air each day to survive. Urban man experiences higher levels of sickness, disability and death from disorders related to breathing and circulation functions than suburban or rural man.



The following paragraphs give the known facts about contaminants associated with the automobile.

- a. Carbon Monoxide: The toxic effects of carbon monoxide on humans have been known and extensively studied for sometime. The primary effect is based on its strong affinity for hemoglobin, with which it combines much more readily than oxygen and forms the carboxy-hemoglobin. The carboxy-hemoglobin reduces the capacity of the blood to transport oxygen from the lungs to the tissues of the body. Concentrations of 30 ppm carbon monoxide for more than four hours under controlled conditions will tie up approximately 5% of body's hemoglobin and produces measureable impairment of physiological functions, such as vision and psychomotor performance. Concentrations higher than 30 ppm carbon monoxide are frequently observed in urban traffic. These effects would be enhanced by any additional illness or exposure which decreases oxygen uptake in the lungs or the ability of the blood and circulatory system to carry and distribute oxygen to the living cells of the body. Cigarette smokers, for example, may have carboxy-hemoglobin levels as high as 8%. An added effect from atmospheric carbon monoxide levels could cause serious health risks (17).
- b. Hydrocarbons: No direct health effect is attributable to hydrocarbons at atmospheric concentrations experienced to date. Certain hydrocarbon derivatives emitted in automobile exhaust may have carcinogenic effects on lung tissue, but the evidence

is inconclusive. The primary concern with these emissions is their indirect effect through participation in the photochemical reactions which lead to the formation of smog. Plant damage, eye and respiratory track irritation and reduced visibility are all associated with the formation and prevalence of photochemical smog.

- c. Oxides of Nitrogen: Oxides of Nitrogen are major participants in photochemical smog reactions. The most significant of these pollutants is nitrogen-dioxide, a yellow-brown gas which significantly reduces atmospheric visibility at low concentrations. It is known to be toxic to man. Deaths and chronic respiratory diseases have resulted from exposure to this gas in mines and in farm silos where it is formed in the decomposition of silage. The low concentrations which occur in the community atmosphere have not been identified as damaging to health, but investigations have not been adequate to determine the significance of this pollutant as a public health problem (18).
- d. Oxidants: Ozone and oxidants resulting from photochemical reactions have damaging effects on materials and vegetation and are irritating to exposed mucous membranes, Eye and respiratory irritations have been reported to occur in sensitive subjects and oxidant levels of 0.1 to 0.15 ppm under conditions prevalent in Los Angeles. Higher levels of oxidant may occur in other locations without producing irritation. Present evidence indicates that within the range of 0.1 to 0.15 ppm oxi-

dant, there can occur interference with athletic performance of school children and impairment of lung function in persons with moderately advanced emphysema. Therefore, the existence of irritation is likely to be an indicator of more serious health hazards. Thus oxidants are associated with the eye irritation, odor, and respiratory effects of photochemical smog (17).

- e. Lead compounds: Lead is known to be toxic to humans, but the concentrations required for this effect, either in the body, or in the environment, have occurred only in isolated cases, usually as a result of occupational hazards. Lead also has some effects which produce no overt symptoms. It interferes with the maturation and development of red blood cells. It affects liver and kidney functions, and disturbs enzyme activity, but neither these nor other bodily disturbances caused by lead have been detected in the general population to date.

## 2. Effect on vegetation:

Plants are useful indicators for air pollutants, and are, indeed, often the first indication that air pollution is becoming a problem. The damaging consequences of air pollution to crops, forests, and ornamental plants has been known for a long time. "Smog" damage to crops is estimated to currently be about to some \$8 million annually in California; motor vehicle emissions are prominent contributors to these losses. Similarly the cost of damage to agricultural crops in the eastern part of the United States has been estimated at \$18 million.

It is believed that this is mostly due to Ozone (15).

Some research has been done about the nature of the factors involved in the action of air pollutants on plants. The relationship between the concentration of air pollutants and the resulting plant injury has been sufficiently well defined so that plants show considerable promise as a measurement of air pollution.

Injury from air contaminants can involve nearly every kind of plants, whether these are wild or domesticated, ornamental or utilitarian, grown for pleasure or as means of livelihood. Large number of substances can damage plants, but sulphur dioxide, "oxidants" and ozone are chief damaging contaminants.

The term "oxidant" covers a variety of unspecified air contaminants having in common the ability to reduce potassium iodide in natural solution. Although ozone is a part of this complex, it is not predominant. "Oxidant" injury to plants is characteristically seen as a silvering, or glazing of the lower leaf surface. This is typical of the plant damage widely seen in the Los Angeles area. It has not been possible to identify the specific constituents in smog responsible for this damage, although peroxyacyl nitrate (PAN) is considered the main constituent.

Ozone, which is catalytically generated in photochemical smog, differs from "oxidant" in the nature of the injury produced on exposed plants; with ozone the upper surface of the leaf is attacked rather than the under surface. Exposures of a few hours at 0.2 part per million result in injury. In the eastern part of this country, extensive damage to tobacco crops has been reported due to ozone (18).

Detailed studies into the mechanisms by which plant injuries are produced by these various toxins are presently underway and should yield fruitful information.

### 3. Material Damage:

A number of specific damaging effects on materials have been identified for automotive emissions. Ozone and other oxidants in photochemical smog attack many materials, including rubber, textiles and dyes. Although often temperature, humidity and rainfall may control the rate and extent of attack, air pollutants from automotive emissions initiate or promote corrosion of metals (6). Paint fails on the metal. Rubber deterioration is due to ozone which forms in polluted air. Even rock, if it is calcareous, is attacked by sulphur-compounds. No firm estimates on total costs to the nation from this damage are available.

## 5. "SOME EFFECTS OF ENGINE-FUEL VARIABLES ON EXHAUST GASES"

Every component of the exhaust gases is more or less affected by the engine-fuel variables. Some of the effects of engine-fuel variables are discussed here.

### 1. Effect on hydrocarbon content:

The presence of hydrocarbons in the engine exhaust is of interest to the automotive industry for two reasons. The first is air pollution and particularly smog formation. The second reason is fuel consumption. Even a small percentage loss of hydrocarbons in the exhaust gases represents a tremendous waste of fuel. Some research has been done on effects of engine-variables on exhaust-gas hydrocarbon content. The following information comes from this research (12).

Investigators have usually divided vehicle operations into four driving conditions: idle, acceleration, cruising and deceleration. Idle and cruising are essentially steady-state conditions, whereas acceleration and deceleration are not.

Idle: Idle is operation of the engine at no load with vehicle stationary. Since the resistance of individual hydrocarbons to oxidation varies with molecular structure, it has been suggested that fuel type might influence the hydrocarbon content of exhaust gases. But the results of the tests show that fuel type has little or no effect either on the total hydrocarbon content in the exhaust or on the amount of unreacted fuel. The most important variable causing the large effect on exhaust-gas hydrocarbon content at idle is the air-fuel ratio as shown in figure 3.

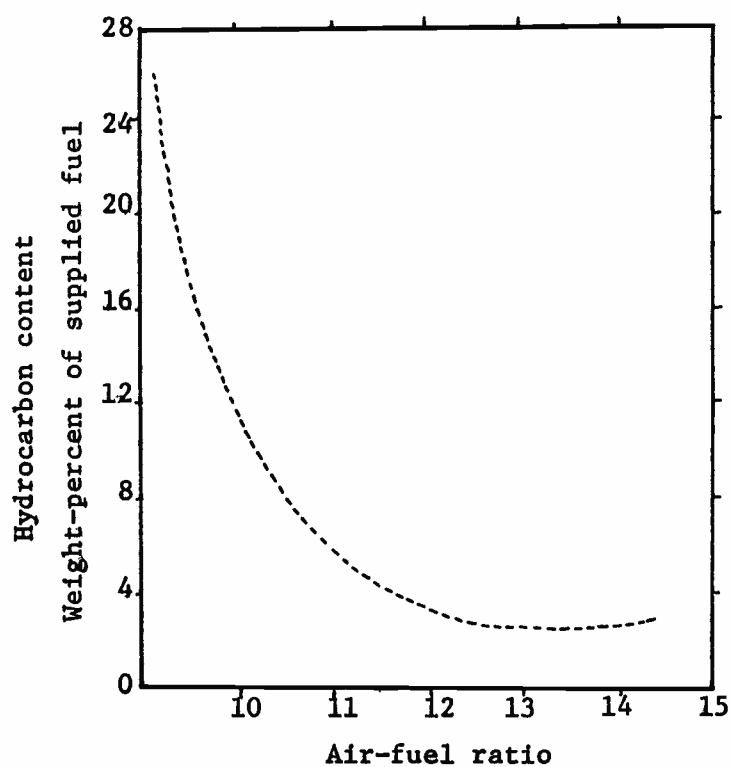


Fig. 3. Effect of Air-fuel ratio on Exhaust-gas hydrocarbon content at idle.

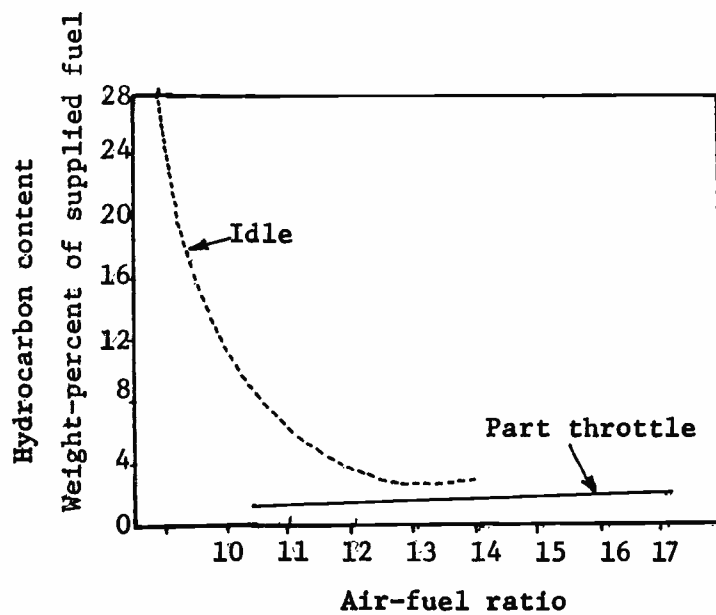


Fig. 4. Effect of Air-fuel ratio on exhaust-gas hydrocarbon at part throttle

Part throttle: This condition includes all the engine operation at power output equal to or greater than road load. Thus both normal cruising and acceleration are included in this part-throttle condition.

1. Fuel-type: The tests show that neither fuel type nor the presence of tetrathyllene has any significant effect on the exhaust gas hydrocarbon content.
2. Air-fuel ratio: As shown in figure 4, contrary to the experience at idle, air fuel ratio has no significant effect on the exhaust gas hydrocarbon content at part throttle.
3. Engine speed: Increase in engine speed has essentially no effect on the exhaust-gas hydrocarbon content at speeds above 1000 rpm.
4. Compression ratio: Examples of the comparative levels of unburned hydrocarbons from a single cylinder engine operating at a series of compression ratios is shown in figure 5.
5. Coolant temperature: The tests indicated that little or no effect on the hydrocarbon content as the coolant temperature was changed.

None of the engine-fuel variables investigated had any significant effect on the exhaust-gas hydrocarbon content at part throttle.

#### Deceleration:

Manifold vacuum: simulated deceleration tests were carried out by coasting downhill at various constant engine speeds at closed throttle. The results of these tests, as well as of some part-throttle tests are illustrated in figure 6. The hydrocarbon content was found to be independent of manifold vacuum below 21 in. of Hg. However, at higher



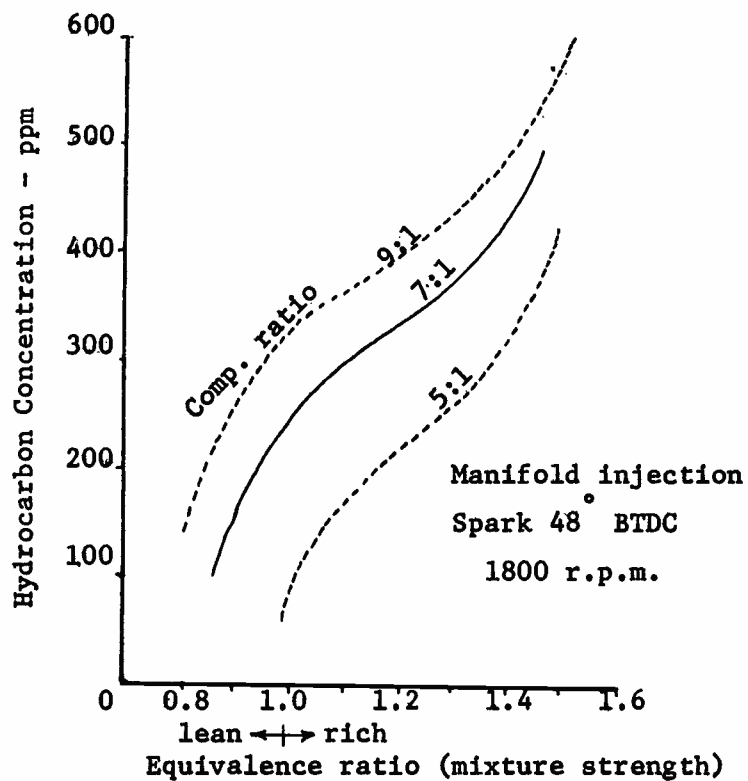


Fig. 5. Influence of compression ratio and mixture ratio on exhaust hydrocarbons. Single cylinder engine.

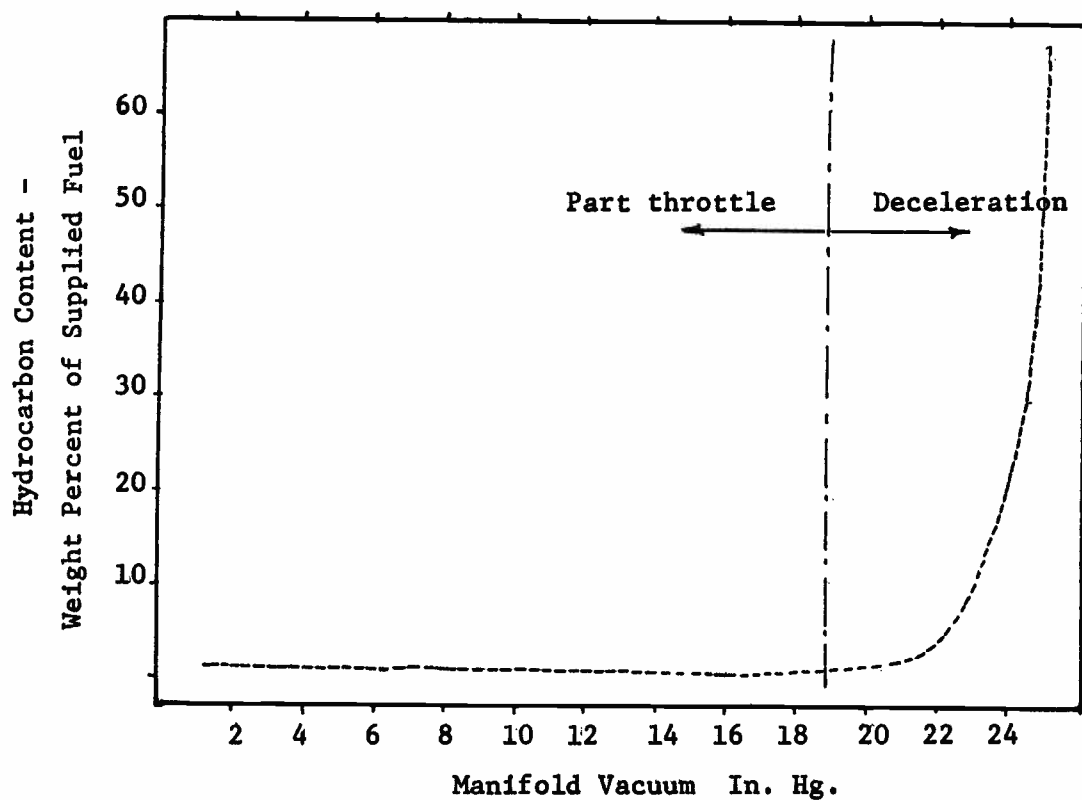


Fig. 6. Effect of intake manifold vacuum on exhaust-gas in hydrocarbon content.

vacuums, the hydrocarbon content increased very rapidly. Flame photography studies by Wentworth and Daniel have shown that these high hydrocarbon contents of high manifold vacuums are due to the failure of the flame to propagate throughout the combustion chamber.

Engine speed: The engine speed affects the exhaust-gas hydrocarbon content as a result of its effect on manifold vacuum.

The ranges of exhaust-gas hydrocarbon contents observed at idle, part throttle and simulated deceleration are shown in table 3.

<u>Table 3. Exhaust gas hydrocarbon content ranges</u>	
<u>Test Condition</u>	<u>Hydrocarbon content Weight % of supplied fuel</u>
Idle	1 to 28
Part throttle	1 to 5
Simulated deceleration	1 to 63

The above table shows that hydrocarbon content is markedly affected by driving condition.

## 2. Carbon monoxide:

Carbon-monoxide concentration in exhaust-gases tends to follow directly the fuel-air ratio as shown in figure 7. Leaning of the mixture results in proportionate reductions in carbon monoxide. It can be seen that the amount of carbon monoxide produced by an engine at any mixture strength is always greater than that calculated for

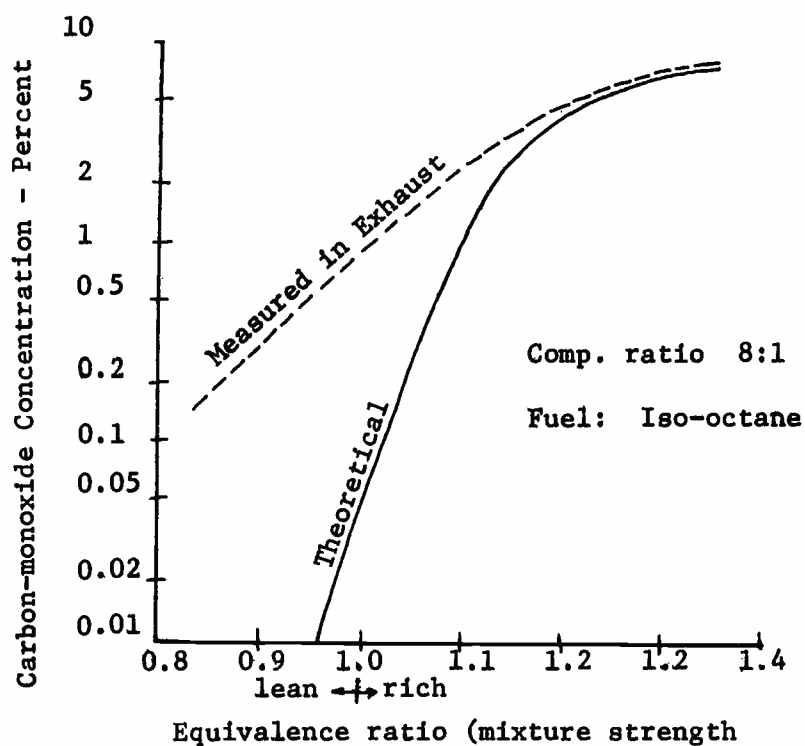


Fig. 7. Theoretical and actual quantities of carbon monoxide in spark ignition engine-exhaust

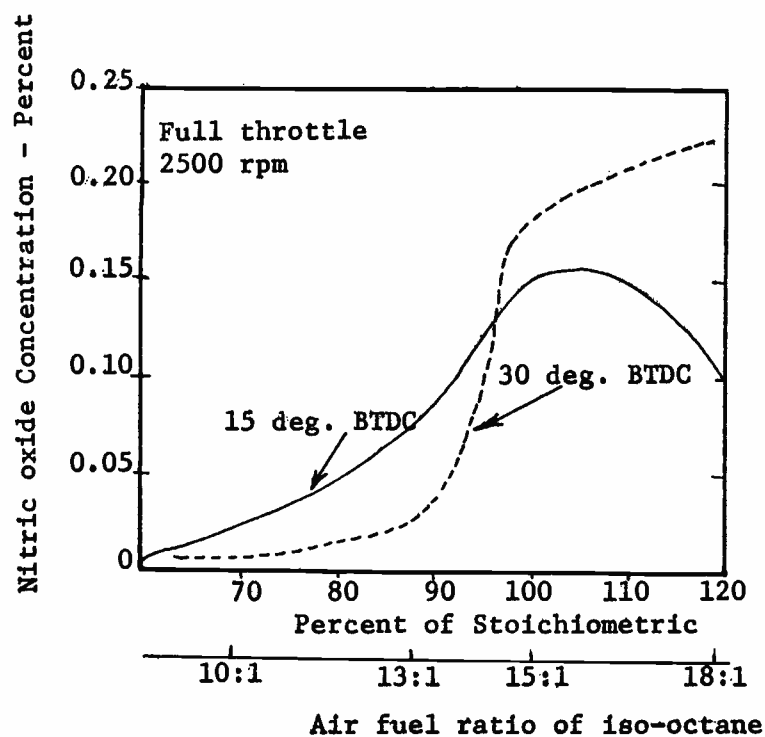


Fig. 8. Correlation of nitric oxide in exhaust with air-fuel ratio at two spark settings.

the moment that the exhaust valve opens. The present explanation for the presence of greater than equilibrium quantities of carbon monoxide is that the reaction rate for conversion of CO to CO<sub>2</sub> is a relatively slow one except at very high temperatures (15).

Carbon monoxide levels from diesel engines are so low as to be no problem.

### 3. Oxides of Nitrogen:

The oxides of nitrogen produced at the engine exhaust port are almost entirely nitric-oxide [NO]. Studies show that nitric oxide always increases with increasing intake pressure. The effect of increasing speed is to reduce the amount of nitric oxide formed because of decrease in reaction time.

Figure 8 correlates percent nitric oxide with air-fuel ratio for two spark settings which bracket optimum engine performance (14). From the figure it is evident that for leaner mixtures nitric oxide concentration for 30 deg. btdc setting is less because of increased time available. At 90% stoichiometric mixture there is sudden increase in nitric oxide concentration in case of 30 deg. btdc setting due to higher temperatures. Above 100% stoichiometric mixture the 15 deg. btdc curve reaches a maximum and starts to decrease because of lower flame temperatures occurring at lean mixtures, with resulting lower reaction rate. Increased time available at 30 deg. btdc results in a continuing mild increase in amount of nitric oxide formed.

Compression ratio has a very significant influence on the amounts of nitric oxide produced. Figure 9 shows the influence of compression

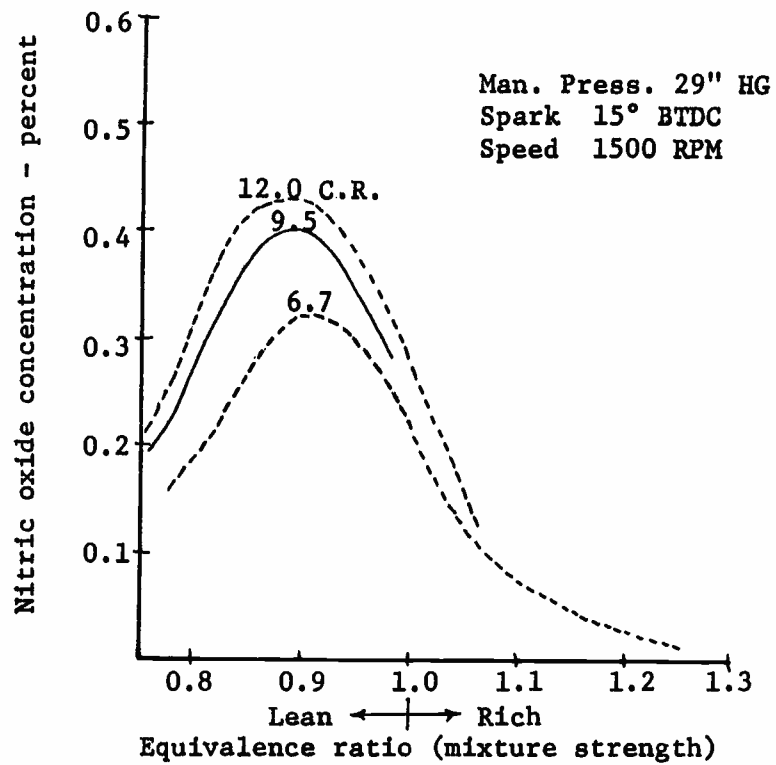


Fig. 9. Influence of compression ratio and mixture ratio on production of nitric oxide from a spark ignition engine.

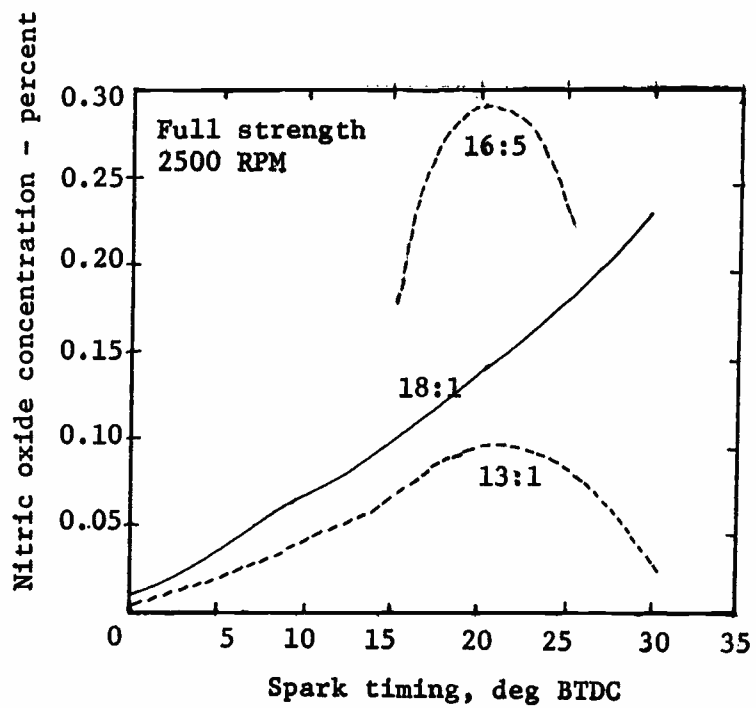


Fig. 10. Correlation of nitric oxide exhaust with spark timing at three air-fuel ratio.

ratio and mixture-ratio on production of nitric oxide from a spark Ignition Engine.

Figure 10 correlates nitric oxide in exhaust gas with spark timing at three air fuel ratios. Spark timing affects both time available and temperatures to which combustion-chamber gases are subjected. At rich mixture as shown by the curve for 13/1 air fuel ratio, there is a gradual increase in nitric oxide production up to optimum spark timing; at more advanced timing the reducing atmosphere tends to destroy nitric oxide previously formed. At slightly lean mixtures as illustrated by a 16/1 air-fuel ratio, the amount formed has increased rapidly near optimum spark timing. It is in this range that rate of fixation is greatest. At lean mixtures, 18/1 and greater, rate of formation is slower because of lower flame temperatures. However, production continues at the more advanced timing because of excess oxygen and increased time available (14).

It is concluded that engines operating under normal spark timings with mixtures on the lean side of stoichiometric mixture will produce appreciable nitric oxide. The amount formed depends most directly on load.

The following table 4 of "typical exhaust gas compositions" will give some idea how the component of exhaust gases vary at different mode of operations (14).

Table 4. Typical Exhaust Gas Compositions.

Mode of operation	Unburned Hydrocarbons PPM	Carbon monoxides vol. percent	Nitrogen oxides PPM	Hydrogen vol. percent	Carbon dioxide vol. percent	Water vol. percent
Idle	750	5.2	30	1.7	9.5	13.0
Cruise	300	0.8	1500	0.2	12.5	13.1
Acceleration	400	5.2	3000	1.2	10.2	13.2
Deceleration	4000	4.2	60	1.7	9.5	13.0

## 6. CONTROL OF AUTOMOTIVE EMISSIONS

Two major sources of air pollution from automotive emission, the crankcase and the exhaust, are now subjected to control.

Crankcase emissions:

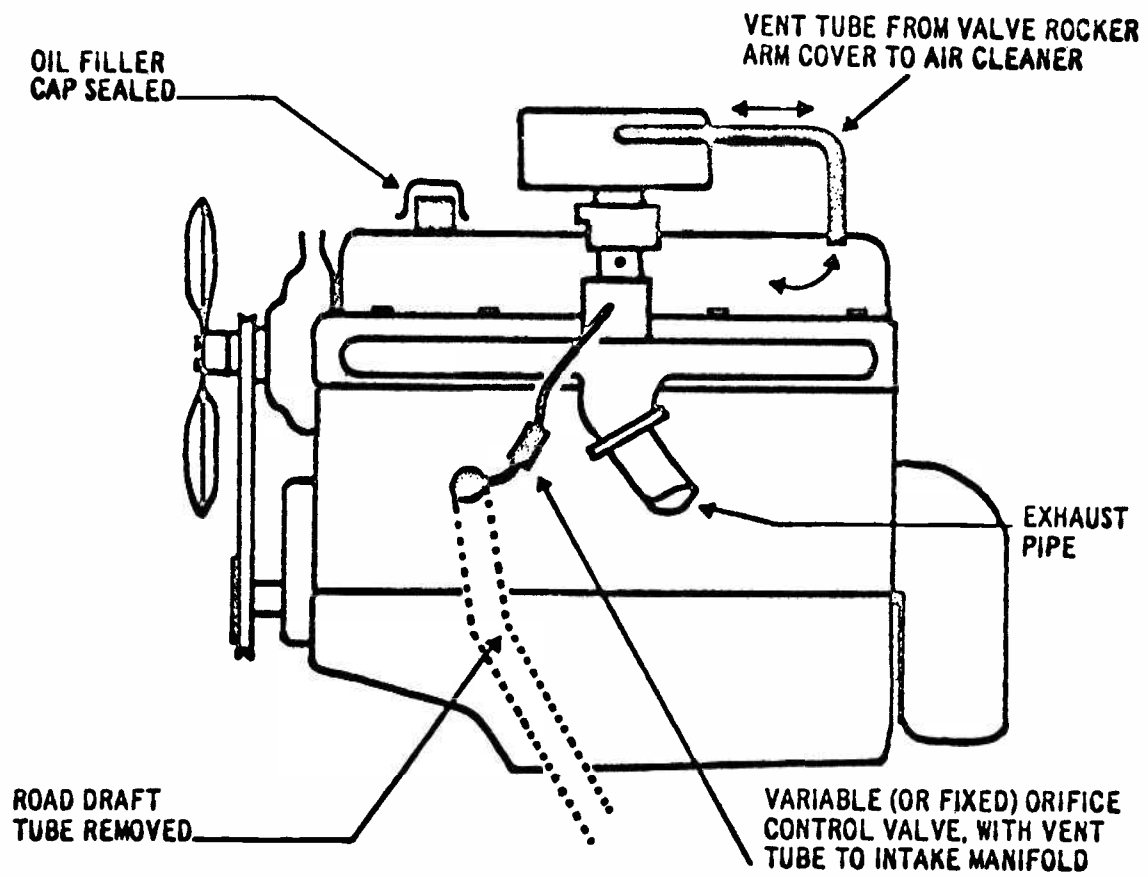
A source of emission which was until recently thought to be unimportant is the crankcase emission. Crankcase emissions are composed of engine blowby gases, ventilation air and crankcase lubricant fumes. Blow-by is the most important and is composed of 70 - 80% fresh air-fuel mixture, the remaining is the residual combustion products from the preceeding cycle.

Poor engine maintenance and the use of poor quality motor oils can greatly increase blow-by.

At idle under the worst conditions the rate of blow-by to exhaust is 1:12. Since only 1/3 of the blow-by is composed of combustion products the CO emission in crankcase emission is considered negligible. On the other hand, for hydrocarbons concentration in the blow-by is 150 ppm vs. 900 ppm in the exhaust, so the blow-by hydrocarbons emission is 1/6 that of exhaust hydrocarbon emission. Control was made mandatory on all 1961 car models offered for sale in California and it has now become nationwide. Luckily there is a relatively easy way to control these emissions (10).

All vehicle manufacturers use substantially the same approach, which involves recycling the gases from the engine oil pump to the combustion chamber as shown in figure 11. Generally the principle of operation is called "positive crankcase ventilation (P.C.V.) (8).





**FIGURE 11 CRANKCASE CONTROL SYSTEM (CLOSED TYPE)**

There are four basic systems:

1. Metering valve actuated by manifold vacuum:

This conducts the crankcase gases to the intake manifold through a variable orifice valve as shown in figure 12, the opening of which is controlled by the intake manifold vacuum. The principal disadvantage is that at open throttle the intake manifold vacuum is insufficient to induce a flow rate large enough to remove all blow-by gases.

2. Metering valve actuated by crankcase vacuum:

This conducts the gases to the intake manifold through a variable orifice valve, the opening of which is controlled by the crankcase vacuum. Ventilation air is admitted to the crankcase through a controlled orifice in the oil filter cap. The flow rate in this system adjusts better to the blow-by rate.

3. A tube to the air cleaner device:

This is essentially just a tube that connects the crankcase to the carburetor air cleaner.

4. Combination systems:

This can be a combination of 1 or 2 with 3. At higher speeds the excess blow-by is returned to the air cleaner. This system can provide positive control at all operating conditions without causing excessive change in the air fuel ratio.

All of these devices have the effect of enriching the air-fuel ratio of the mixture. If not taken into account and corrected it

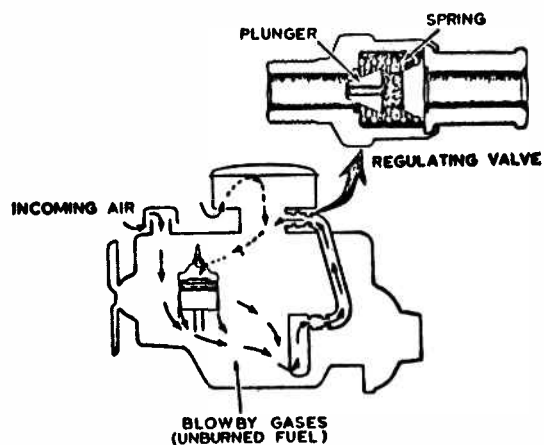


Fig. 12. Positive crankcase ventilation system for control of crankcase emissions

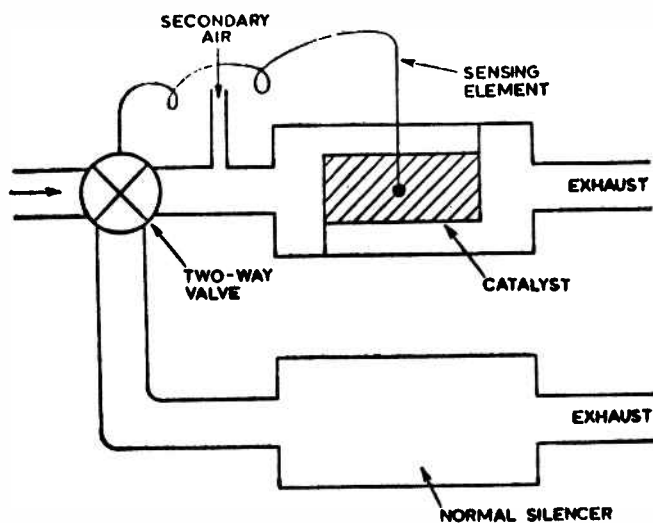


Fig. 13 Schematic diagram of catalytic system with bypass

will increase the CO and the hydrocarbons in the exhaust. This can be corrected easily in the design of new cars but adaption to used cars may create a problem.

#### Exhaust emissions:

Well over 150 different chemical components have been isolated from auto exhaust. The troublesome ones that occur in greatest concentrations are carbon monoxide, the unburned hydrocarbons, and the oxides of nitrogen.

The Los Angeles air pollution board has established motor vehicle exhaust emission standards for hydrocarbons and carbon monoxide in exhaust gases of 275 ppm hydrocarbons and 1.5% CO as referred to a specific set of vehicle operating conditions. A recent survey of 194 vehicles selected to be typical of California vehicles in terms of make, age and previous condition of service, yielded an average of 960 ppm hydrocarbon and 3.1% CO. The absolute hydrocarbon emission from the exhaust was 6% by weight of supplied fuel. Individual vehicles may vary from less than 2% to more than 20% (2).

Table 4 shows some analyses of exhaust gases for various operating conditions.

The control of these exhaust gases has not been solved completely. There are three basic approaches to this problem: modification of engine design and operation, catalytic devices and direct flame devices.

Induction devices for exhaust control include a variety of devices for modifying the carburation or ignition system. The principal reductions have been obtained by changes in carburetor metering, ignition

timing and control of manifold vacuum during deceleration. Limitations of manifold vacuum can be accomplished by control of throttle opening, utilizing either special control devices, throttle return dash pots or retarded idle ignition timing to increase the required throttle opening during idle and thereafter during deceleration (2).

In 1967 the Chrysler Corporation utilized engine adjustment and operational modification alone to accomplish emission control to meet the presently existing standards. Figure 14 illustrates how this is done through a combination of modifications called the "Cleaner Air Package". The other major domestic automobile manufacturers utilize a combination of engine modification and air injection into the exhaust as illustrated in figure 15 and 16 (18).

The second method using catalytic devices is the one that appears to offer the most advantages and is the one that is most often proposed. It consists essentially of a catalyst bed set in the muffler to promote the oxidation of hydrocarbons and carbon monoxide (5).

Some of the advantages given for a catalyst system over the competitive systems are

1. No additional fuel is necessary to control or sustain the reaction.
2. Temperature is lower, thus reducing construction material problems.
3. Self-initiating at low temperature (200 C for good catalysts), and needs no spark plugs or other similar devices to sustain the reaction.

FIGURE 14

## CHRYSLER CLEANER AIR PACKAGE - SCHEMATIC

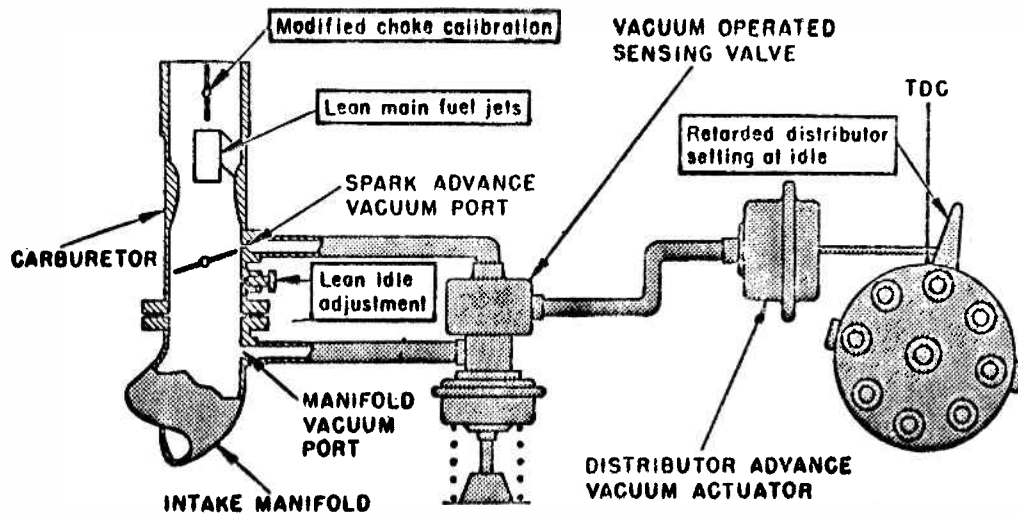


FIGURE 15

## GM AIR INJECTION

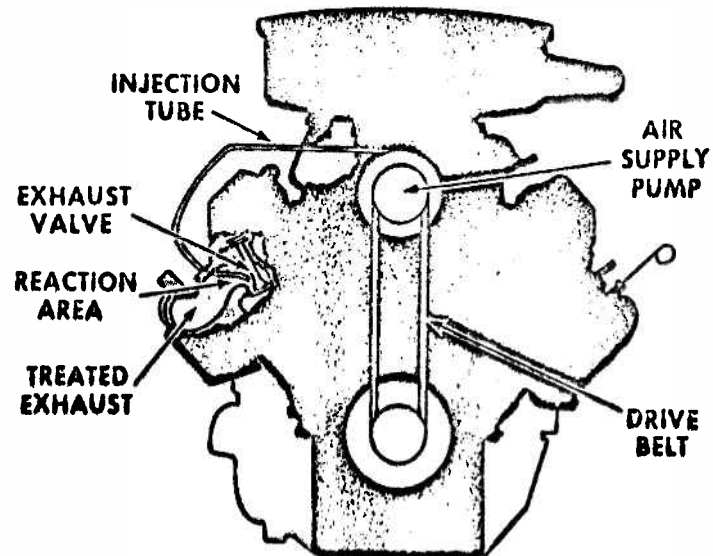
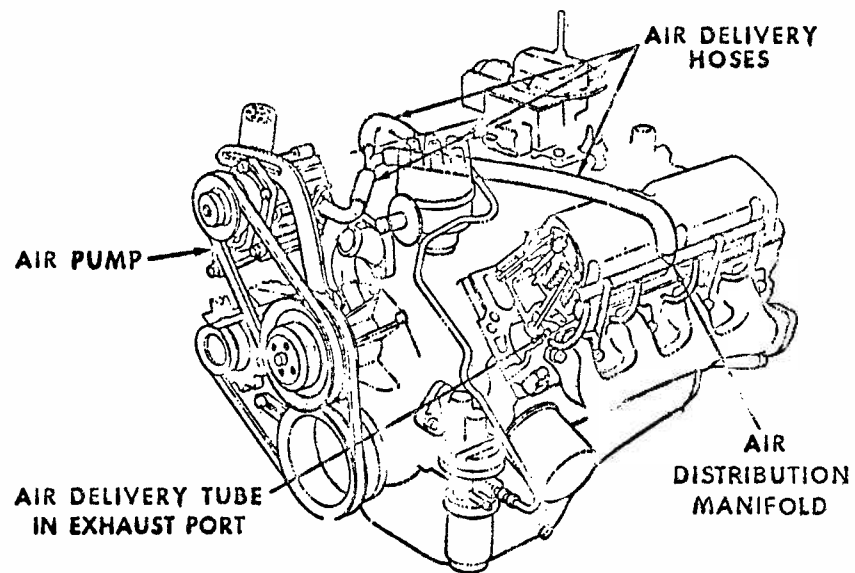


FIGURE 16  
FORD THERMACTOR EXHAUST EMISSION  
CONTROL SYSTEM



4. Operates satisfactorily with low levels of hydrocarbon and carbon monoxide content.

Some of the usual oxidation catalysts are copper, manganese, cobalt, noble metals such as platinum and palladium. These catalysts are supported on substances such as porcelain, corundum, pumice and aluminum silicate.

A schematic diagram of catalytic system is illustrated in figure 13. The catalytic converter must have accessory equipment in addition to the catalyst bed and container. One of these is a means of providing an additional air supply. This can be either with a pump or venturi. A pump offers more positive control while the venturi is less expensive and gives less trouble. The control must also be equipped with a thermally activated bypass system to protect the device from high temperatures under severe driving conditions, for example in mountain driving.

There are several design requirements which cause trouble in design. If the reactor is too well insulated to conserve heat and improve its performance, it may overheat. If not insulated, then its cold start performance suffers. At the present time the maximum permissible bed temperatures for catalysts is 800 C (5).

Non-flame after burners can be designed to give various degrees of reduction of both hydrocarbons and carbon monoxide concentrations in exhaust gases. However, many problems of vehicle compatibility, size and weight, durability, catalyst life, odors, excessive heat and cost must be resolved before these become practical (1).

The third method of control is what is commonly known as flame



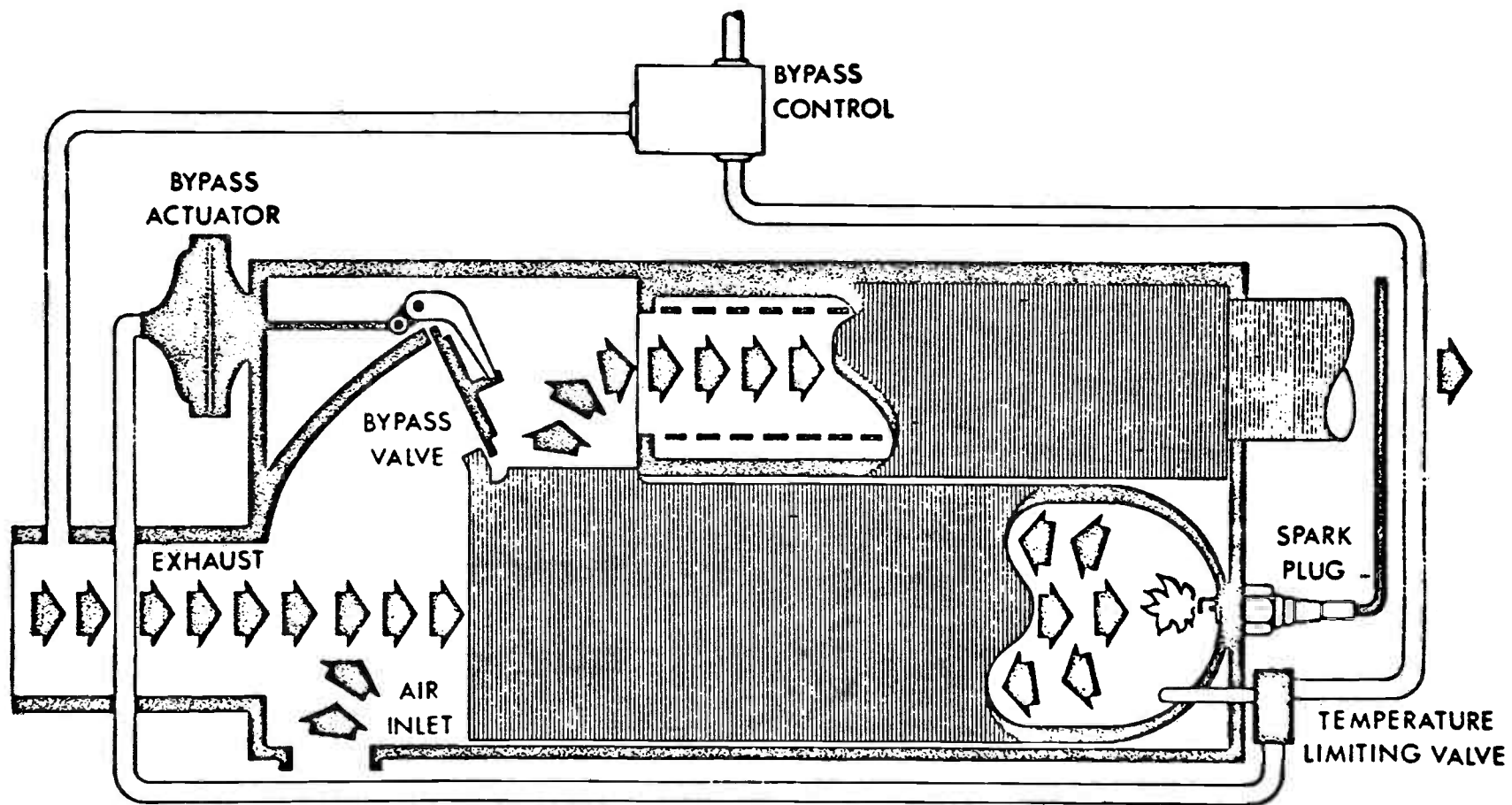


FIGURE 17 DIAGRAM OF A FLAME AFTERBURNER  
 Developed by American Machine and Foundry Corp. under license from Chromalloy Corp.

after burner. Flame-type afterburner as illustrated in figure 17 requires that the exhaust stream contain sufficient combustibles so that when mixed with additional air, the mixture is within the limits of flammability. Since the flame afterburners have many of the problems in common with non-flame afterburners as mentioned above plus the additional fuel requirements to sustain the flame, these devices aren't particularly attractive.

It is possible to have a non-flame non-catalyst type burner but it must be very near the engine or employ elaborate and costly exchangers and insulation to conserve heat.

The typical flame afterburner is a combustion chamber in the area of the muffler. A spark ignition system is provided along with an air supply and thermal bypass. It is often necessary to improve the combustibility by heat exchange, the addition of extra fuel or both.

#### Evaporative Loss Control:

Several control systems have now been proposed and demonstrated which produce substantial reductions in evaporative losses. But in many instances the evaporative loss control systems tend to increase exhaust emissions. But the volatile hydrocarbons are not a significant source when compared to the other sources of vehicle emissions (15).

#### Oxide of Nitrogen:

Exhaust control devices for oxides of nitrogen have not yet been installed on motor vehicles. Several methods for accomplishing this have been investigated, including water injection, exhaust recircula-

tion, operating the engine at low air-fuel ratios and catalytic reduction.

Exhaust recycling or exhaust recirculation has been most widely suggested methods of control. In this system 10 to 20% of the exhaust gas is withdrawn from the exhaust manifold or exhaust pipe and with suitable flow controls is introduced in the intake manifold of the engine. This reduces peak cycle temperatures in the cylinder, and the burning rate is decreased, with significant reductions in nitrogen oxide emissions. However, problems still remain. The amount of recirculation is critical; too much increases the hydrocarbon and carbon monoxide and can cause losses in vehicle performance, power, economy and driveability. Exhaust recirculation and lean mixture operation for hydrocarbon and carbon monoxide control appear to be entirely incompatible. A combination of exhaust recirculation with air injection permits simultaneous control of hydrocarbons, carbon monoxide and nitrogen oxides (9).

#### Diesel emission control:

Diesel-powered vehicles constitute only a small fraction of the total vehicle pollution but their exhaust can be seen and smelled. A number of basic and applied research studies are now underway in an effort to reduce the highly undesirable characteristics of these emissions.

Present technology is adequate to allow a large reduction in diesel smoke. Potential control methods include:

fuel additives

adherence to high quality fuel specifications

engine rating below the smoke limit

engine turbo supercharging

proper maintenance

driver training to reduce driver abuse of vehicles

fumigation

dilution

Studies aimed at modification or reduction of diesel odor have only begun, but it appears that solutions will be forthcoming. Several additives for odor reduction are under development. Also, additives can be used to mask or change the odor. Catalytic converters may also be used to change unpleasant and irritating characteristics to a sweet smelling odor (18).

The carbon monoxide content of diesel engine exhaust is quite low. If required, catalytic converters or other systems could be used to reduce this level even further. Unburned hydrocarbons in diesel engines are also low, and these might be further reduced by adapting several of the techniques presently available for gasoline engines.

The total quantity of nitrogen oxides from the diesel-powered truck on the highway may be high in comparison to that of the private auto in residential operation. Some reduction is possible, but it will not be accomplished easily. The recycling technique used to reduce nitrogen oxides in gasoline engine exhaust probably will not be effective with diesels. Catalytic converters may be useful, but if control

is desired, additional studies to develop techniques to reduce these emissions in diesel equipment will be necessary.

It appears possible to reduce diesel smoke and odor to acceptable levels, and to control other diesel pollutants with the possible exception of nitrogen oxides. This should cause no problems. Since they are normally low compared to the pollutants from gasoline engines and should be susceptible to further reduction with conventional methods.

Other types of engines and other propulsion methods:

Because of the difficulty of eliminating the pollutants in the exhaust of existing vehicles, there is much interest in other types of engine and in using propulsion systems that do not discharge pollutants which cause the present problems. Stratified charge, diesel and gas turbine engines, rotary engines, fuel cells and electric vehicles are examples of other engines or motive power suggested from time to time.

All engines burning conventional fuels would be sources of pollutants. Except for the diesel, there are few data on just what the emission would be. To be attractive for air pollution control purposes, however, the engines must either have very low emissions or be easily controlled to produce low emissions.

- a. Rotary engines: The rotary-type ignition engine, such as the Wankle engine, does not compare favorably at present in exhaust emissions with the reciprocating engine. Oil consumption in the rotary engine is high, and blow-by is directed into exhaust, resulting in increased concentra-

tion of emissions at lower engine speeds. No information is available on the nitrogen oxide emissions from this type of engine.

- b. Gas turbine: It seems that this engine has about the lowest emissions of the various internal combustion engines, even though exhaust volume is high. On this basis, the gas turbine appears to be an attractive means for reducing air pollution. Data are not available from which to decide if the emissions, without control systems, are low enough to meet all possible requirements. Also, little is known about control systems that might be needed if the emission levels were found to be not satisfactory.
- c. Stratified charge engine: In the stratified charge engine, fuel is injected into only part of the intake air near the spark plug in the cylinder. The overall fuel-air ratio can be quite lean and the compression ratio of the engine can be increased over that of the conventional reciprocating engine. The design of the engine is such that the air introduction quenches combustion around the edges of the flame, producing high hydrocarbon output. Nitrogen oxide levels are also high, but carbon-monoxide concentrations as low as 0.15% appear possible.
- d. Improvement in present engine: It is not certain at this time that any internal combustion engine would prove superior (for air pollution purposes) to the conventional engine

modified to discharge low quantities of pollutants. Recent studies have indicated that it may be possible to reduce hydrocarbon concentrations from the piston engine to under 50 ppm. If the engines could also be made to operate at high air-fuel ratios, low concentrations of oxides would be expected.

- e. Batteries and Fuel cells: Electric-powered vehicles would not produce the pollutants that are now of so much concern and would appear to be ideal for solving air pollution problems. Many technical problems must be solved before it can be concluded that such vehicles could replace all or large part of present type engines (17).

#### Fuels:

##### Fuel composition:

It is difficult to demonstrate the significant effects on exhaust emission and the advent of practical devices for blow-by elimination and evaporation control. These two sources of unburned hydrocarbons are directly related to fuel composition, since they consist primarily of unburned fuel. The engine combustion process can alter hydrocarbon composition, however, and only a marginal reduction in reactive exhaust hydrocarbons is obtainable by lowering the quantity of reactive hydrocarbons in gasoline.

Data concerning competitive gasolines marketed in the Los Angeles area indicated that while the aromatic and olefin content of gasolines

varied over a wide range, the effect on both total exhaust hydrocarbons emissions and the more reactive exhaust hydrocarbon olefins was not large.

Data concerning the effect of fuel volatility and composition on evaporation losses indicate that removal of  $C_4-C_6$  olefins from a commercial gasoline reduces the reactivity of evaporation losses by about 65%. A reduction in fuel volatility might simplify the fuel system modifications required.

#### Fuel additives:

A great number of substances, serving a number of purposes, are added to today's gasolines. The principal additives from a quantitative standpoint are anti-knock compounds, but other classes include deposit modifiers, antioxidants, metal deactivators, antirust agents, detergents, and lubricants. None of the additives currently in gasoline were originally developed to reduce engine emissions.

Lead alkyls have been used in motor gasoline for over 40 years to improve octane rating. Lead has no immediate and direct effect on exhaust emissions or their reactivity, but it has been related to combustion chamber deposits which increase hydrocarbon emissions.

The catalyst devices certified for use in California were designed against specific targets of effectiveness and cost. Possibly more effective catalyst devices could be developed for operation on leaded gasolines but they would probably be more expensive. Experimental work reported on a catalyst device to reduce unburned hydrocarbon,



carbon monoxide, and nitrogen oxides to very low levels indicates that an unleaded and low sulphur gasoline will be required.

Considerable research has been directed to the search for additives to modify combustion chamber deposits to reduce or eliminate their adverse effect on exhaust emissions. Success in this area is not likely (18).

#### Combustion improvers:

No gasoline additives in commercial use today produce a significant reduction in exhaust emissions, but a considerable effort has been made to find such an additive. Some compounds appear to reduce unburned hydrocarbons by 5-10% when used at relatively high concentrations of up to 1%. The more effective of these additives also increase nitrogen oxides, indicating that the mechanism probably involves an increase in peak combustion temperatures.

This work has been abandoned because the small beneficial effect was not deemed significant relative to the large reductions desired. Chances are very slim for commercialization of an effective combustion modifier in the next few years, but if exhaust emissions are first reduced to low levels by other means, further improvements with gasoline additives may become practical.

#### Diesel antismoke additive:

In recent years a diesel fuel anti-smoke additive containing barium has been sold by several manufacturers. A few oil companies supply finished diesel fuel containing this additive or package it for spot

usage. The increased cost to the consumer for the use of this additive is from one to two cents per gallon of fuel. Visible smoke can be eliminated with the additive if the initial level is light or medium, but it is less effective in reducing heavy smoke output to acceptable levels.

The additive is reported to reduce ring-wear by up to 50% and it also extends injector life. Other reports indicate buildup of deposits caused by barium, but the effect of the deposits has not been proven to be harmful to the engine. Metallic barium is toxic, but it appears that the sulphur levels normally present in most diesel fuels are sufficient to convert it to harmless barium-sulphate.

#### Alternative fuels:

Several suggestions have been made that use of fuels other than leaded gasoline might help alleviate the photochemical smog problem. The most persistent suggestion is replacement of gasoline with liquefied petroleum gases (LPG), which are essentially propane and butane. The reasoning behind this suggestion is that the exhaust constituents emitted from vehicles using LPG will be of a non-smog forming nature. However, even if this is so, the limited supply and other economic problems and safety problems tend to make the proposed solution unfeasible (6).

Another proposal envisages the use of high-quality non-leaded gasoline in conjunction with a catalytic converter. This solution is probably technically feasible, but again, economic problems are formidable.

Recently the Ethyl Corporation has announced a new anti-knock compound. The compound, called Ak-33X, is methyl cyclopentadienyl manganese tricarbonyl. The compound is still under test, but it could aid in the solution of the auto exhaust problem.

## Summary

Automobile emissions cause an air pollution problem primarily in the Los Angeles area and in other metropolitan areas. However, legislation may make control devices mandatory nationwide even where they are not needed now.

The present cost goal for the exhaust control devices to be installed on new cars is \$50 per year which should include amortization of the capital costs and necessary maintenance. The cost to place one on a used car, if it is possible, would be much higher. The crankcase emission control devices have a yearly replacement cost of about \$4.00; on the used car cost of installation may run \$15.00 - \$20.00.

The installation of the crankcase emission control devices should provide a marked reduction in hydrocarbon and CO emissions from auto exhausts. The problem of control of the exhaust emissions is much more difficult but although a method exists, it appears to have many operating problems and the cost is relatively high. The control of the problem will probably take many years to accomplish. Since it is difficult if not impossible to provide all the various sizes and types for all used cars, probably the most that can be expected is a gradual improvement as the older cars are replaced with new cars equipped with the devices.

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#### ACKNOWLEDGEMENT

The author wishes to express his sincere gratitude for the encouragement and valuable guidance offered by Professor A. H. Duncan, Department of Mechanical Engineering, Kansas State University, during preparation of this report.

AIR-POLLUTION DUE TO  
AUTOMOTIVE EMISSION

by

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B. E. (Mech.) Gujarat University, India, 1967

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AN ABSTRACT OF A MASTER'S REPORT

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Mechanical Engineering

KANSAS STATE UNIVERSITY  
Manhattan, Kansas

1968



The purpose of this report is to discuss the causes, effects and control of air pollution due to automotive emission. Air pollution presents an increasingly serious threat to the health and welfare of people in areas of large population. One principal contributor to this pollution is the emission of carbon monoxide, hydrocarbons, nitrogen oxide and lead components from the exhaust of automotive emission.

Engine exhaust system discharges comprise a major part of the air-pollutants, which are the result of automotive emission. Another important emission path is through the engine crankcase. Crankcase emissions are composed of (1) engine blow-by gases (2) ventilation air and (3) crankcase lubricant fumes. Emission also comes from evaporation of gasoline from the tank or the carburetor.

The harmful effects of air pollution due to automotive emission on human health, vegetation and property are discussed. Some effects of engine-fuel variables on exhaust gases are also discussed. As pollutants are discharged from more than one point in each vehicle, different methods of control may be needed for each point. Some of these control methods and their advantages and disadvantages are discussed. To control the air-pollution, due to automotive emission, the most promising suggestion is replacement of gasoline with liquified petroleum gases (LPG) which are essentially propane and butane. But limited supply and other economic and safety problems tend to make this proposed solution unfeasible.

At last one should not forget that the total emission of pollutants from a single vehicle is not very large. It is the concentration of a great number of vehicles that creates the problem.